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54 Modified elastomer and laminate thereof.

57 Modified polymer compositions comprising elastomers blended with not more than 50 parts by weight of a crystalline polyolefin are prepared by reaction of the polymers with an unsaturated carboxylic acid or its acid anhydride. The modified composition optionally containing a filler, is particularly suitable for laminating to metals and other polymers; laminates show superior hot water resistance, salt water resistance and thermal shock resistance.

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1 This invention relates to a modified elastomer,
2 and a laminate comprising said modified elastomer. More
3 specifically, this invention relates to a modified elas-
4 tomer having high adhesion to metals, polyolefins, poly-
5 amides, polyesters, polyvinyl chloride or polyvinyl
6 alcohol, and a laminate of the modified elastomer having
7 superior hot water resistance, salt water resistance and
8 thermal shock resistance.

9 The accompanying drawing is a graph showing the
10 relation of the amount of the unsaturated carboxylic acid
11 added to the effect produced in the present invention.

12 Heretofore, in order to improve the corrosion
13 resistance or appearance of metals, various synthetic
14 resins have been coated on the inside and outside sur-
15 faces of metal tubes, metal plates, wires, etc., or in
16 order to remedy the defects of various synthetic resins,
17 laminates of these resins bonded to other resins have
18 been suggested. As such synthetic resin materials, poly-
19 olefins which are inexpensive and have various excellent
20 physical and chemical properties have attracted attention
21 as laminates with metals or other synthetic resins. Since
22 polyolefins are inherently non-polar, their affinity for
23 metals or various synthetic resins is small, and they have
24 the defect of being unable to be easily bonded to metals
25 and synthetic resins. Various methods have therefore been
26 suggested in order to remedy this defect.

27 For example, there have been proposed a laminate
28 composed of a metal and a polyolefin bonded through a
29 modified polyolefin having an unsaturated carboxylic acid
30 such as maleic anhydride graft-copolymerized therewith
31 (Japanese Patent Publication No. 10757/67); a method for
32 obtaining a laminated sheet by co-extruding nylon and a
33 polyolefin modified with an unsaturated carboxylic acid
34 or its anhydride (Japanese Patent Publication No.
35 43055/76); a method for improving the adhesion strength
36 of polyolefins which comprises adding 1 to 20% by weight
37 of a rubber compound to a crystalline polyolefin and

1 modifying it with an unsaturated carboxylic acid or its
2 anhydride (Japanese Laid-Open Patent Publication No.
3 8035/77); and a method which comprises laminating a com-
4 position comprising 70 to 98% by weight of a crystalline
5 polyolefin and 30 to 2% by weight of a copolymer of an
6 α -olefin and modified ethylene having maleic anhydride
7 graft-polymerized therewith or a modified polyolefin
8 resulting from reaction of a mixture of 70 to 98% by
9 weight of a crystalline polyolefin and a copolymer of
10 ethylene and an α -olefin with an unsaturated carboxylic
11 acid or its anhydride, to a polyamide, a polyester or a
12 saponified product of an ethylene/vinyl acetate copolymer
13 (Japanese Laid-Open Patent Publication Nos. 82/79 and
14 83/79).

15 The modified polyolefins whose adhesion strength
16 has been increased by these methods, however, decrease in
17 adhesion strength within short periods of time upon con-
18 tact with electrolyte-containing water such as sea water
19 or saline solution or with heated liquids or upon being
20 subject to temperature change, and peel from the bonded
21 surface. Furthermore, their adhesion strength is still
22 not entirely sufficient in application to co-extrusion and
23 blow molding which require higher adhesion strength. In
24 order to have the adhesiveness of the modified polyolefins
25 exhibited, high temperatures of about 200°C are usually
26 required in the processing step, and a huge cost of energy
27 is spent. It is desired therefore to decrease the pro-
28 cessing temperature. Modified polymers and their use in
29 laminates are broadly disclosed in United States Patent
30 3,862,265 (R. A. Steinkamp, et al) wherein critical extru-
31 sion conditions were required in order to effect said
32 modification. In addition, the reference did not recog-
33 nize the need to control the concentration of unsaturated
34 carboxylic acid or its anhydride and the level of crys-
35 talline polyolefin in order to achieve the very high
36 adhesion levels, hot water resistance, salt water resis-
37 tance and thermal shock resistance demonstrated in the

1 present invention.

2 In accordance with the present invention,
3 it has been found that a product obtained by selecting an
4 ethylene/butene-1 copolymer, a styrene/butadiene copolymer
5 or an ethylene/propylene copolymer as an elastomer, and
6 modifying 100 parts by weight of the elastomer with 0.005
7 to 0.8 part by weight of an unsaturated carboxylic acid or
8 its acid anhydride shows a very high adhesion strength.
9 This discovery has led to the present invention.

10 Thus, the present invention provides (1) a modi-
11 fied elastomer resulting from addition reaction of 100
12 parts by weight of at least one elastomer selected from
13 an ethylene/butene-1 copolymer, a styrene/butadiene co-
14 polymer and an ethylene/propylene copolymer or 100 parts
15 by weight of a mixture of at least one said elastomer and
16 not more than 50 parts by weight of a crystalline poly-
17 olefin, with 0.005 to 0.8 part by weight of an unsaturated
18 carboxylic acid or its anhydride; and (2) a laminate com-
19 prising (A) a modified elastomer resulting from addition
20 reaction of 100 parts by weight of at least one elastomer
21 selected from an ethylene/butene-1 copolymer, a styrene/
22 butadiene copolymer and an ethylene/propylene copolymer
23 with 0.005 to 0.8 part by weight of an unsaturated car-
24 boxylic acid or its anhydride, or (B) a modified elastomer
25 resulting from addition reaction of 100 parts by weight of
26 a mixture of at least one said elastomer and not more than
27 50 parts by weight of a crystalline polyolefin with 0.005
28 to 0.8 part by weight of an unsaturated carboxylic acid or
29 its anhydride, or (C) a composition comprising (A) or (B)
30 and a filler, and a material selected from the group con-
31 sisting of metals, polyamides, polyesters, polyvinyl
32 chloride and polyvinyl alcohol.

33 The elastomer used in this invention is an
34 ethylene/butene-1 copolymer, an ethylene/propylene co-
35 polymer, a styrene/butadiene copolymer, or mixtures
36 thereof. Desirably, it has a tensile strength of at
37 least 60 kg/cm², especially at least 100 kg/cm². When

1 the tensile strength of the elastomer itself is low, it is
2 desirable to increase it by adding a crystalline polyole-
3 fin such as polyethylene, polypropylene, polybutene-1 or
4 mixtures thereof. The ethylene/butene-1 copolymer pre-
5 ferably has an ethylene content of 10 to 90% by weight,
6 especially 70 to 85% by weight, and a Mooney viscosity
7 (ASTM D927-57T; the same applies hereinbelow) of 10 to
8 200 at 100°C. The styrene(S)/butadiene(B) copolymer is,
9 for example, a random copolymer such as styrene butadiene
10 rubber (SBR), SBS-type block copolymer or BSB-type block
11 copolymer of styrene and butadiene having a styrene con-
12 tent of 5 to 70% by weight, preferably 20 to 40% by weight,
13 and a Mooney viscosity of 10 to 200 at 100°C. A styrene/
14 butadiene block copolymer having the SBS-type block struc-
15 ture and a high tensile strength is especially preferred.
16 The ethylene/propylene copolymer preferably has an ethy-
17 lene content of 10 to 90% by weight, especially 30 to 80%
18 by weight, a Mooney viscosity of 10 to 200 at 100°C and
19 a density of 0.85 to 0.90.

20 The crystalline polyolefin used in this inven-
21 tion includes homopolymers of olefins or copolymers of
22 different kinds of olefins, such as high-density poly-
23 ethylene, medium-density polyethylene, low-density poly-
24 ethylene, crystalline ethylene/propylene copolymer, crys-
25 talline ethylene/butene-1 copolymer, polypropylene, crys-
26 talline propylene/ethylene copolymer, polybutene-1 and
27 poly(4-methyl-pentene-1). Mixtures of two or more of
28 these polymers or copolymers may be used. High-density
29 polyethylene, low-density polyethylene and polypropylene
30 are especially preferred among them.

31 Examples of the unsaturated carboxylic acids or
32 the anhydrides thereof include acrylic acid, methacrylic
33 acid, fumaric acid, maleic acid, maleic anhydride, citra-
34 conic acid, citraconic anhydride, itaconic acid, itaconic
35 anhydride, endo-bicyclo-[2.2.1]-1,4,5,6,7,7-hexachloro-
36 5-heptene-2,3-dicarboxylic acid, endo-bicyclo-[2.2.1]-1,
37 4,5,6,7,7-hexachloro-5-heptene-2,3-dicarboxylic anhydride,

1 endo-bicyclo-[2.2.1]-5-heptene-2,3-dicarboxylic acid,
2 endo-bicyclo-[2.2.1]-5-heptene-2,3-dicarboxylic anhydride,
3 cis-4-cyclohexene-1,2-dicarboxylic acid, and cis-4-cyclo-
4 hexene-1,2-dicarboxylic anhydride. Of these, maleic
5 anhydride, acrylic acid, and endo-bicyclo-[2.2.1]-5-
6 heptene-2,3-dicarboxylic anhydride are especially pre-
7 ferred.

8 The amount of the unsaturated carboxylic acid
9 or its anhydride is 0.005 to 0.8 part by weight, prefer-
10 ably 0.1 to 0.7 part by weight, per 100 parts by weight
11 of the elastomer composed of at least one of the ethylene/
12 butene-1 copolymer, styrene/butadiene copolymer and ethy-
13 lene/propylene copolymer or a mixture of it with the crys-
14 talline polyolefin. If the amount of the unsaturated
15 carboxylic acid or its anhydride is less than 0.005 part
16 by weight, the adhesion strength of the resulting product
17 is not sufficient. If, on the other hand, it exceeds 0.8
18 part by weight, the peel strength of the resulting product
19 decreases. By maintaining the amount of the unsaturated
20 carboxylic acid low as in the present invention, the for-
21 mation of an increased amount of a gel-like product, in-
22 creased coloration, etc. can be inhibited.

23 The modified elastomer of this invention can be
24 produced by adding the unsaturated carboxylic acid or its
25 anhydride to the elastomer comprising at least one member
26 of the group consisting of ethylene/butene-1 copolymer,
27 styrene/butadiene copolymer and ethylene/propylene copoly-
28 mer or a mixture of said elastomer with the crystalline
29 polyolefin and applying various known modifying methods.
30 For example, it can be obtained by adding the unsaturated
31 carboxylic acid or its anhydride with or without a radical
32 generator, for example an organic peroxide such as diter-
33 tiary butyl peroxide, dicumyl peroxide or benzoyl peroxide,
34 to the elastomer composed of at least one of the aforesaid
35 ethylene/butene-1 copolymer, styrene/butadiene copolymer
36 and ethylene/propylene copolymer, mixing them in a mixer
37 such as Henschel mixer, ribbon blender, V-shaped blender

1 or tumbler, and melting and kneading the mixture at 120
2 to 300°C, preferably 180 to 250°C, in a Banbury mixer, or
3 a single-screw or multi-screw extruder. Alternatively, it
4 can be obtained by dispersing the aforesaid copolymer
5 substrate and the unsaturated carboxylic acid or its an-
6 hydride in water or an organic solvent, and heating the
7 dispersion in the presence of the aforesaid radical gene-
8 rator or a water-soluble peroxide.

9 The mixing proportions of the ethylene/butene-1
10 copolymer, styrene/butadiene copolymer or ethylene/propy-
11 lene copolymer, and the crystalline polyolefin are such
12 that the amount of the former is at least 50 parts by
13 weight, preferably at least 70 parts by weight, and the
14 amount of the latter is not more than 50 parts by weight,
15 preferably not more than 30 parts by weight. If the
16 amount of the crystalline polyolefin exceeds 50 parts by
17 weight per 50 parts by weight of the ethylene/butene-1
18 copolymer, styrene/butadiene copolymer, or ethylene/propy-
19 lene copolymer, the characteristics of the modified elas-
20 tomer are lost, and the effect of improving the adhesion
21 of the elastomer is not sufficient. In particular, the
22 hot water resistance, salt water resistance and thermal
23 shock resistance of the product are inferior. The amount
24 of the organic peroxide is not more than 0.1 part by
25 weight, preferably 0.001 to 0.08 part by weight, per 100
26 parts by weight of the ethylene/butene-1 copolymer, sty-
27 rene/butadiene copolymer or ethylene/propylene copolymer
28 or a mixture of the copolymer with the crystalline poly-
29 olefin.

30 Desirably, the resulting modified elastomer is
31 used alone. It is possible however to use it after adding
32 to it an unmodified elastomer or crystalline polyolefin
33 or a mixture of these. Such a product can be produced,
34 for example, by mixing 0.005 to 0.8 part by weight, pre-
35 ferably 0.1 to 0.7 part by weight, of the unsaturated
36 carboxylic acid or its anhydride and less than about 0.1
37 part by weight, preferably 0.001 to 0.08 part by weight,

1 of an organic peroxide with 100 parts by weight of an
2 elastomer comprising at least one member of the group con-
3 sisting of ethylene/butene-1 copolymer, styrene/butadiene
4 copolymer and ethylene/propylene copolymer or a mixture of
5 the elastomer with the crystalline polyolefin, and knead-
6 ing the mixture at a temperature of 120 to 300°C, prefer-
7 ably 180 to 250°C, mixing the resulting modified elastomer
8 and an unmodified elastomer or a crystalline polyolefin
9 in a mixer such as a ribbon blender, V-shaped blender,
10 tumbler or Henschel mixer, and melting and kneading the
11 mixture at 120 to 250°C in a Banbury mixer, or a single-
12 screw or multi-screw extruder. In the modified elastomer
13 composition composed of the modified elastomer and the
14 unmodified elastomer or crystalline polyolefin, the mixing
15 ratio of the individual ingredients can be selected as
16 desired according to the purpose of use. If the amount of
17 the unmodified elastomer or crystalline polyolefin in-
18 creases, the properties of the modified elastomer will be
19 lost and the improvement of adhesiveness is not sufficient.
20 In particular, the hot water resistance, salt water resis-
21 tance and thermal shock resistance of the resulting compo-
22 sition become inferior. The amount of the unmodified
23 elastomer or crystalline polyolefin added is not more than
24 100 parts by weight, preferably not more than 43 parts by
25 weight, per 100 parts by weight of the modified elastomer.
26 However, when the modified elastomer contains the crys-
27 talline polyolefin, the amount of the crystalline poly-
28 olefin is desirably decreased so that the total amount of
29 the crystalline polyolefin contained in 100 parts by
30 weight of the modified elastomer composition is not more
31 than 50 parts by weight. If required, the modified elas-
32 tomer or elastomer composition may contain various fillers
33 such as calcium carbonate, white carbon, carbon black,
34 absorbers, various stabilizers, antistatic agents, mold
35 releasing agents, lubricants, pigments, etc.

36 The metal used in the laminate of this inven-
37

1 tion includes, for example, aluminum, copper, zinc, nickel,
2 iron, tin, stainless steel, brass, tin-plated iron, and
3 galvanized sheet steel. The polyamide is a polymer having
4 recurring units of an acid amide (-CONH-) and obtained by
5 ring-opening polymerization of a lactam, polycondensation
6 of an aminocarboxylic acid, or polycondensation of a
7 diamine with a dibasic acid. It is called Nylon by the
8 tradename. Examples are Nylon 6, Nylon 66, Nylon 11,
9 Nylon 12 and Nylon 6, 10. The polyester is a polymeric
10 compound having an ester linkage in the main chain of the
11 molecule, and is usually obtained by polycondensation
12 between a dibasic acid and a dihydric alcohol. Examples
13 are polyethylene terephthalate and polybutylene terephtha-
14 late. Polyvinyl chloride is a homopolymer of a vinyl
15 chloride monomer alone or a copolymer resulting from co-
16 polymerization of a vinyl chloride polymer with another
17 monomer such as vinyl acetate, and is of various grades
18 such as the soft, hard, and high impact grades. Polyvinyl
19 alcohol is a water-soluble resin obtained by saponifying
20 polyvinyl acetate having a degree of polymerization of
21 1200 to 2000. A polymer under the tradename Vinylon is an
22 example of a polymer starting from this resin.

23 The laminate in this invention is obtained by
24 melt lamination of the aforesaid modified elastomer or
25 modified elastomer composition and a material selected
26 from the aforesaid metals, polyamides, polyesters, poly-
27 vinyl chloride, polyvinyl alcohol and polyolefins. The
28 method of lamination is not particularly limited. There
29 can be utilized known methods, such as a method which com-
30 prises forming the individual components into films or
31 sheets and bonding them under heat and pressure, a method
32 which comprises laminating them outside a die, a method
33 which comprises laminating them inside a die, or a method
34 which comprises extrusion and coating them in laminated
35 layers. Basically, the laminate of the present invention
36 has a two-layer structure in which the modified elastomer
37 or modified elastomer composition is laminated to a

1 material selected from the metals, polyolefins, poly-
2 amides, polyesters, polyvinyl chloride and polyvinyl
3 alcohol, and a three-layer structure in which the modified
4 elastomer or modified elastomer composition is sandwiched.
5 Depending upon uses, various other combinations can be
6 used so long as they include the basic constituent ele-
7 ments.

8 The modified elastomer or modified elastomer
9 composition in accordance with this invention shows good
10 adhesion to the aforesaid metals or resins, and a laminate
11 having a high adhesion strength can be made. The adhesion
12 surface of the laminate has markedly improved hot water
13 resistance, salt water resistance and thermal shock resis-
14 tance over laminates having the conventional modified
15 polyolefin as an interlayer.

16 The resin laminate obtained by this invention
17 is useful as a packaging film or sheet, bottles, containers,
18 etc. by taking advantage of its gas impermeability, mois-
19 ture resistance, oil resistance, etc. It can also be
20 used as an interlayer in coating a metal such as a wire,
21 cable, metal plate, metal tube and other metal inserts.
22 In this case, the modified elastomer or its composition
23 of this invention is adhered to the metal to be coated or
24 a sheet made of the modified elastomer or its composition
25 is wrapped around it. A molded article containing the
26 metal and having a high adhesion strength can be obtained
27 by setting the assembly in a mold and molding a polyolefin
28 therein.

29 Examples 1 to 21 and Comparative Examples 1 to 3

30 An ethylene/butene-1 copolymer (abbreviated C₂⁼-
31 C₄⁼-1 hereinbelow) having an ethylene content of 77% by
32 weight, a melt index (ASTM D-1238E, the same applies here-
33 inbelow; abbreviated MI) of 4.0 (190°C) and a density of
34 0.89, an SBS-type styrene/butadiene block copolymer (to be
35 abbreviated SBR hereinbelow) having a styrene content of
36 40% by weight, an MI of 2.6 (190°C) and a density of 0.95,
37 an ethylene/propylene rubber (to be abbreviated EPR here-
38

1 inbelow) having an ethylene content of 74% by weight, an
2 MI of 1:9 (190°C) and a density of 0.88, low-density poly-
3 ethylene [density=0.919, MI=10.0 (190°C); to be abbrev-
4 viated LDPE hereinbelow], high-density polyethylene
5 [density=0.961, MI=8.0 (190°C); to be abbreviated HDPE
6 hereinbelow], maleic anhydride, endo-bicyclo-[2.2.1]-5-
7 heptene-2,3-dicarboxylic anhydride (to be abbreviated
8 dicarboxylic anhydride-H hereinbelow), and ditertiary
9 butyl peroxide (to be abbreviated DTBP hereinbelow) were
10 mixed in the proportions shown in Table 1 by a Henschel
11 mixer at room temperature. The mixture was fed into a
12 vent-equipped extruder having a screw diameter of 65 mm,
13 and extruded at 230°C to form cylindrical pellets.

14 The resulting pellets of the modified elastomer
15 were formed into a 0.2 mm-thick sheet by a hot press form-
16 er at 200°C and 40 kg/cm². A three-layer structure com-
17 posed of an aluminum sheet/the modified elastomer sheet/
18 aluminum sheet was prepared from the resulting sheet and
19 0.1 mm-thick aluminum sheets by melt-bonding at a pre-
20 treating and bonding temperature of 80°C, 100°C and 200°C,
21 respectively, under a pressure of 40 kg/cm² for 2 minutes.
22 The three-layer laminate was cut to a width of 25 mm, and
23 its 90° peel strength was measured by an Instron universal
24 tensile tester. The results are shown in Table 1.

25 The laminate was also tested for hot water re-
26 sistance, salt water resistance and thermal shock resis-
27 tance using samples prepared by processing a two-layer
28 laminate of the aforesaid modified elastomer and a phos-
29 phoric acid-treated iron plate (JIS G-3141, 0.7 mm x 70 mm
30 x 120 mm) in the same way as in the preparation of the
31 laminate for measurement of delamination peel strength.
32 The thickness of the modified elastomer was 0.15 mm.

33 (1) Test for hot water resistance

34 A cross hatch, 60 mm long, reaching the metal
35 was provided in the modified elastomer layer of the two-
36 layer laminate using a sharp knife, and the laminate was
37 immersed in hot water at 60°C. The time (days) which

1 elapsed until the water permeated from the cross hatch
2 to an extent of 2 mm was measured, and defined as the
3 durable time.

4 (2) Test for salt water resistance

5 The same cross hatch as in the sample for the
6 hot water resistance test was provided, and the two-layer
7 laminate was immersed in a 3% aqueous solution of sodium
8 chloride at 50°C. The time (days) which elapsed until the
9 salt water permeated from the cross hatch to an extent of
10 2 mm was measured, and defined as the durable time.

11 (3) Thermal shock resistance

12 The two-layer laminate was subjected to a cycle
13 of room temperature (30 minutes) 50°C (2 hours) room
14 temperature (30 minutes) -30°C (2 hours) room
15 temperature, and the number of cycles which was repeated
16 until the modified elastomer layer peeled off from the
17 zinc phosphate-treated iron plate was determined, and
18 defined as cycles of thermal shock resistance. The
19 results are shown in Table 1.

Properties of the modified elastomer

TABLE I

Properties of the modified elastomer															
Starting resin		Modifier		TABLE I											
Elastomer		Polyolefin		Unsaturated carboxylic acid or its anhydride		DTBP		Amount of un-saturated acid added (wt.%)		90° Peel strength (kg/25 mm)			Adhesion strength durability		
Type	Amount (parts by weight)	Type	Amount (parts by weight)	Type	Amount (parts by weight)	Amount (parts by weight)	Amount (parts by weight)	Amount (parts by weight)	Amount (parts by weight)	Aluminum sheet, bonded at 80°C	Aluminum sheet, bonded at 100°C	Aluminum sheet, bonded at 200°C	Hot water resistance (days/60°C)	Salt water resistance (days/NaCl, 50°C)	Thermal shock resistance (cycles/-30°C, 50°C)
1	OX-C ₁ -1	100	—	Maleic anhydride	0.05	0.07	0.04	2.40	2.65	2.80	2.90	2.90	>50	10	>20
2	"	100	—	"	0.1	0.07	0.08	2.40	2.65	2.80	2.90	2.90	>50	>10	>20
3	"	100	—	"	0.3	0.07	0.25	2.60	2.80	2.80	>30	>30	>50	>10	>20
4	"	100	—	"	0.6	0.07	0.48	2.60	2.82	2.82	>30	>30	>50	>10	>20
5	"	100	—	"	0.8	0.08	0.65	1.50	1.80	1.80	2.60	2.60	45	7	>20
6	"	100	—	Maleic anhydride	0.1	0.07	0.07	2.35	2.60	2.60	2.80	2.80	50	10	>20
7	"	100	—	"	0.2	0.07	0.14	2.50	2.70	2.70	>30	>30	>50	>10	>20
8	"	100	—	"	0.5	0.08	0.32	2.60	2.80	2.80	>30	>30	>50	>10	>20
9	"	100	—	"	0.8	0.08	0.55	1.80	2.00	2.00	2.70	2.70	50	>10	>20
10	SBR	100	—	Maleic anhydride	0.3	0.01	0.27	2.60	2.85	2.85	>30	>30	>50	>10	>20
11	"	100	—	Maleic anhydride	0.5	0.01	0.35	2.65	2.95	2.95	>30	>30	>50	>10	>20
12	"	100	—	Acrylic acid	0.5	0.01	0.40	2.60	2.80	2.80	>30	>30	>50	>10	>20
13	EPR	100	—	Maleic anhydride	0.3	0.06	0.23	2.00	2.45	2.45	2.80	2.80	>50	>10	>20
14	C ₁ -C ₁ -1	90	HDPE	"	0.3	0.07	0.25	1.80	2.20	2.20	2.80	2.80	50	8	>20
15	"	80	"	"	0.3	0.07	0.24	1.60	2.00	2.00	2.50	2.50	50	8	>20
16	"	80	LDPE	"	0.3	0.07	0.24	1.60	2.00	2.00	2.50	2.50	45	5	>20
17	"	70	"	"	0.3	0.07	0.21	1.00	1.95	1.95	2.30	2.30	>50	9	>20
18	SBR	80	HDPE	"	0.3	0.01	0.25	1.60	2.35	2.35	2.70	2.70	>50	>10	>20
19	O ₂ -C ₁ -1	75	EPR	"	0.3	0.07	0.24	2.10	2.40	2.40	2.80	2.80	>50	>10	>20
20	"	50	"	"	0.3	0.07	0.23	1.70	2.00	2.00	2.40	2.40	>50	>10	>20
21	"	25	"	"	0.3	0.07	0.24	1.20	1.40	1.40	1.70	1.70	>50	>10	>20
Comp. Ex.	"	100	—	Maleic anhydride	1.5	0.08	1.0	6.0	10.0	10.0	19.0	19.0	40	5	1.5
2	"	100	—	"	3.0	0.10	2.0	3.0	5.0	5.0	16.0	16.0	30	3	8
3	"	100	—	"	5.0	0.10	3.0	2.0	4.0	4.0	13.0	13.0	20	1	3

TABLE 1 (Cont.)

Example	Amount of un-saturated acid added (wt.%)	90° Peel strength (kg/25 mm)			Adhesion strength durability		
		Aluminum sheet, bonded at 80°C	Aluminum sheet, bonded at 100°C	Aluminum sheet, bonded at 200°C	Hot water resistance (days/60°C)	Salt water resistance (days/3% NaCl, 50°C)	Thermal shock resistance (cycles/-30°C, 50°C)
1	0.04	24.0	26.5	22.0	>50	10	>20
2	0.08	24.0	26.5	22.0	>50	>10	>20
3	0.25	26.0	28.0	>30	>50	>10	>20
4	0.40	26.0	28.2	>30	>50	>10	>20
5	0.65	15.0	18.0	26.0	45	7	>20
6	0.07	23.5	26.0	22.0	50	10	>20
7	0.14	25.0	27.0	>30	>50	>10	>20
8	0.32	26.0	28.0	>30	>50	>10	>20
9	0.55	18.0	20.0	27.0	50	>10	>20
10	0.27	26.0	28.5	>30	>50	>10	>20
11	0.35	26.5	29.5	>30	>50	>10	>20
12	0.40	26.0	28.0	>30	>50	>10	>20
13	0.23	6.0	8.0	10.0	>50	>10	>20
14	0.25	20.0	24.5	22.5	>50	>10	>20
15	0.24	18.0	22.0	28.0	50	0	>20
16	0.24	16.0	20.0	25.0	50	0	>20
17	0.21	10.0	12.5	25.0	45	5	>20
18	0.25	16.0	23.5	27.0	>50	9	>20
19	0.24	21.0	24.0	28.0	>50	>10	>20
20	0.23	17.0	20.0	24.0	>50	>10	>20
21	0.24	12.0	14.0	17.0	>50	>10	>20
Comparative Example 1	1.0	6.0	10.0	12.0	40	5	15
2	2.0	3.0	5.0	16.0	30	3	0
3	3.0	2.0	4.0	13.0	20	1	3

Example 22

Using modified $C_2=C_4-1$ having varying amounts of maleic anhydride grafted thereto obtained by varying the amount of maleic anhydride added in Example 1, a three-layer laminate of aluminum sheet/modified $C_2=C_4$ /aluminum sheet was prepared at a bonding temperature of 100°C and 200°C, respectively, by the same method as in Example 1. The 90°C peel strength of the three-layer laminate was measured by the same method as used in Example 1, and the results are shown in Figure 1. In the figure (A) represents the results obtained with the laminate bonded at a temperature of 100°C, and (B) represents the results obtained with the laminate bonded at 200°C. * shows that the aluminum sheet broke.

It is seen from the figure that the laminate obtained when the amount of maleic anhydride grafted was less than about 0.65% by weight (the amount of maleic anhydride added was 0.8% by weight or less) have a high peel strength.

Comparative Examples 4 to 7

Each of polypropylene [MI=1.0 (230°C), density 0.90; to be abbreviated PP hereinbelow], a propylene/ethylene block copolymer [ethylene content 7% by weight, MI=1.0 (230°C), density 0.90; to be abbreviated P/E block hereinbelow], ethylene/propylene rubber [ethylene content 74% by weight, MI=1.9 (190°C), density 0.88; to be abbreviated EPR hereinbelow], HDPE used in Example 6, and LDPE used in Example 8 in the proportions indicated in Table 2 was modified in the same way as in Example 1. Each of the modified polyolefins was laminated to form test specimens in the same way as in Example 1, and tested for 90°C peel strength, and adhesion durability represented by hot water resistance, salt water resistance and thermal shock resistance. The results are shown in Table 2.

TABLE 2

Com- para- tive Ex- ample	Starting resin		Modifier			Properties of the modified polyolefin						
	Type	Amount (parts by weight)	Unsaturated carboxylic acid:anhydride	DTBP	Amount of the un- saturated acid grafted (wt. %)	90° Peel strength (kg/25 mm)			Adhesion strength durability			
			Type			Amount (parts by weight)	Amount (parts by weight)	Bonded to an aluminum sheet at 80°C	Bonded to an aluminum sheet at 100°C	Bonded to an aluminum sheet at 200°C	Hot water resistance (days/60°C)	Salt water resistance (days/3 % NaCl, 50°C)
4	PP	100	Dicarboxylic anhydride-H	1.0	0.3	0.30	Adhesion did not occur	Adhesion did not occur	4.0	0.1	0.05	2
5	P/E block	100	"	1.0	0.3	0.40	"	"	5.0	0.2	0.05	2
6	LDPE	100	Maleic anhydride	0.3	0.06	0.27	"	"	3.0	0.5	0.05	5
7	HDPE/ EPR	70/30	"	0.3	0.07	0.22	"	"	5.0	5	0.5	10

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1 Examples 23 to 28 and Comparative Examples 8 to 11

2 $C_2=C_4$ -1 and ethylene/butene-1 copolymer modi-
3 fied with maleic anhydride (to be abbreviated MA-modified
4 $C_2=C_4$ -1 of Example 1, maleic anhydride-modified
5 styrene/butadiene block copolymer (to be abbreviated MA-
6 modified SBR hereinbelow) of Example 3, the dicarboxylic
7 anhydride-H modified styrene/butadiene block copolymer
8 (to be abbreviated HA-modified SBR hereinbelow) of Example
9 4, HDPE used in Example 6, modified HDPE (to be abbreviated
10 MAHDPE hereinbelow) obtained by modifying the aforesaid
11 HDPE by the same method as in Example 1, LDPE used in
12 Example 8, and PP having an MI of 5.0 and a density of 0.90
13 were mixed in the proportions shown in Table 3 in a Henschel
14 mixer at room temperature. The mixture was fed into a
15 vent-equipped extruder having a screw diameter of 65 mm,
16 and extruded at 230°C to form a modified elastomer compo-
17 sition in the form of cylindrical pellets.

18 Test specimens were prepared from the modified
19 elastomer composition by the same method as in Example 1,
20 and tested for 90° peel strength durability represented
21 by hot water resistance, salt water resistance and thermal
22 shock resistance. The results are shown in Table 3.

TABLE 3

	Modified elastomer composition				Properties of the modified elastomer composition						
	Modified elastomer		Polyolefin		90° Peel strength (kg/25 mm)			Adhesion strength durability			
	Type	Amount (parts by weight)	Type	Amount (parts by weight)	Bonded to aluminum sheet at 80°C	Bonded to aluminum sheet at 100°C	Bonded to aluminum sheet at 200°C	Hot water resistance (days/50°C)	Salt water resistance (days/3% NaCl, 50°C)	Thermal shock resistance (days/-30°C, 50°C)	
1											
2											
3	E										
4	X										
5	A										
6	M										
7	P										
8	L										
9	E										
10	23	MA-modified $C_2^{\overline{w}}-C_4^{\overline{w}}-1$	80	PP	20	14.0	20.0	26.0	45	7	> 20
11	24	"	80	HDPH	20	15.0	20.5	27.0	45	7	> 20
12	25	"	80	LDPE	20	14.0	10.0	25.0	45	7	> 20
13	26	"	50	HDPH	50	3.0	6.0	18.0	20	3	> 20
14	27	MA-modified BPR	80	"	20	14.0	22.0	28.0	50	9	> 20
15	28	MA-modified BPR	80	"	20	13.0	22.0	27.5	50	8	> 20
16	COMP	MA-modified $C_2^{\overline{w}}-C_4^{\overline{w}}-1$	30	"	70	No adhesion occurred.	1.0	20.0	5	0.05	10
17	EX.	MA-modified HDPH	60	$C_2^{\overline{w}}-C_4^{\overline{w}}-1$	40	"	0.5	8.0	4	0.1	10
18	9	"	80	"	20	"	No adhesion occurred.	5.0	2	0.05	4
19	10	"	20	"	80	"	"	6.0	10	0.5	15
20	11	"	20	"	80	"	"	6.0	10	0.5	15

Examples 29 to 32 and Comparative Examples 12 and 13

Three-layer laminates of various metals or resins as shown in Table 4 were prepared by the same method as in Example 1 using the modified elastomer composition of Examples 1, 6, 10 and 13 and the modified polyolefins of Comparative Examples 2 and 4. The 90° peel strength of each of these three-layer laminates was measured. The results are shown in Table 4.

TABLE 4

		Example 29	Example 30	Example 31	Example 32	Comparative Example 12	Comparative Example 13
1	Adhesive resin	Modified elastomer of Example 1	Modified elastomer of Example 6	Modified elastomer of Example 10	Modified elastomer of Example 13	Modified polyolefin of Comparative Example 2	Modified polyolefin of Comparative Example 5
2							
3							
4							
5							
6							
7							
8	90° Peel strength (kg/25 mm)						
9	LDPE	Not peelable	5.0	Not peelable	7.0	1.5	Not peelable
10	HDPE	"	6.0	"	8.5	1.5	"
11	PP	2.5	2.0	2.5	2.0	Not peelable	3.0
12	E/P block copolymer	4.5	3.0	6.0	3.5	"	4.5
13	Nylon-6	6.5 ⁽⁺⁾	6.0 ⁽⁺⁾	4.5 ⁽⁺⁾	5.0 ⁽⁺⁾	2.0	3.0
14	Nylon-6,6	6.7 ⁽⁺⁾	6.0 ⁽⁺⁾	4.5 ⁽⁺⁾	5.0 ⁽⁺⁾	2.0	3.0
15	lined PVC	1.8	2.0	1.6	1.7	3.0	3.0
16	High Impact PVC	8.0	10.0	4.0	9.5	No adhesion occurred	No adhesion occurred
17	Soft PVC	1.5	4.0	1.0	3.5	"	"
18	Vinylon	1.5 ⁽⁺⁾	1.5 ⁽⁺⁾	1.5 ⁽⁺⁾	1.5 ⁽⁺⁾	2.0	1.5
19	PBT	3.0	3.5	3.0	3.0	No adhesion occurred	No adhesion occurred
20	PBT	4.0	4.0	4.0	4.0	"	"
21	Aluminum sheet	3.0 ⁽⁺⁾	3.0 ⁽⁺⁾	2.9	2.8	5	4
22	Steel sheet	2.5	2.7	2.3	2.5	6	5
23	Steel sheet (treated with ZnPO ₄)	5.0	4.8	4.3	4.2	1.5	2
24	Galvanized steel sheet	2.5	2.6	2.2	2.3	6	5
25	Tin plate	2.0	2.1	1.6	1.5	5	5
26	Copper Sheet	2.0	2.3	2.1	2.2	5	4
27	Stainless steel sheet	2.5	2.4	2.1	2.1	6	5

WHAT WE CLAIM IS:

1. A modified elastomer prepared by the reaction of:

(A) 100 parts by weight of at least one elastomer selected from an ethylene/butene-1 copolymer, a styrene/butadiene copolymer and an ethylene/propylene copolymer, or

(B) 100 parts by weight of a mixture of at least one said elastomer and not more than 50 parts by weight of a crystalline polyolefin; with

(C) 0.005 to about 0.8 part by weight of an unsaturated carboxylic acid or its anhydride.

2. A modified elastomer according to claim 1 wherein said crystalline polyolefin is selected from high-density polyethylene, medium-density polyethylene, low-density polyethylene, crystalline ethylene/butene-1 copolymer, polypropylene, crystalline propylene/ethylene copolymer, polybutene-1 and poly (4-methyl-pentene-1), or mixtures thereof.

3. A modified elastomer according to claim 2 wherein said crystalline polyolefin is selected from high-density polyethylene, low-density polyethylene and polypropylene.

4. A modified elastomer according to claims 1-3 further prepared by the reaction of a radical generator.

5. A modified elastomer according to claim 4 wherein said radical generator is an organic peroxide.

6. A modified elastomer according to claims 1-5 wherein said unsaturated carboxylic acid or anhydride thereof is selected from maleic anhydride, acrylic acid and endobicyclo-[2.2.1]-5-hentane-2,3-dicarboxylic anhydride.

7. A laminate comprising:

(A) a modified elastomer according to claims 1-6 resulting from the reaction of 100 parts by weight of at

least one elastomer selected from an ethylene/butene-1 copolymer, a styrene/butadiene copolymer and an ethylene/propylene copolymer with 0.005 to about 0.8 part by weight of an unsaturated carboxylic acid or its anhydride, or

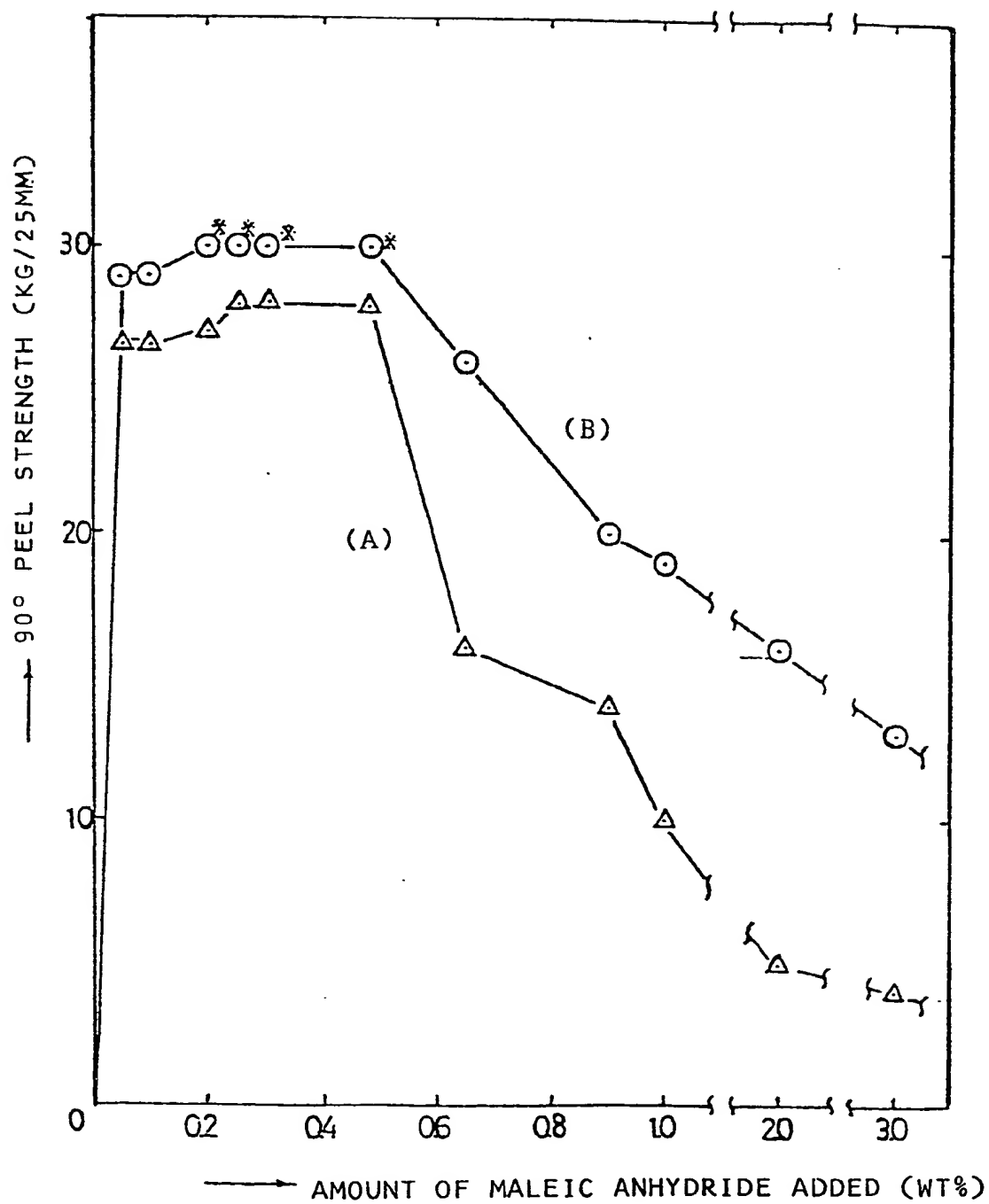
(B) a modified elastomer according to claims 1-6 resulting from addition reaction of 100 parts by weight of a mixture of at least one said elastomer and not more than 50 parts by weight of a crystalline polyolefin with 0.005 to about 0.8 part by weight of an unsaturated carboxylic acid or its anhydride, or

(C) a composition comprising (A) or (B) and a filler; and

(D) a material selected from metals, polyamides, polyesters, polyvinyl chloride and polyvinyl alcohol.

8. A laminate according to claim 7 wherein said metal is selected from aluminum, copper, zinc, nickel, iron, tin, stainless steel, brass, tin-plated iron, and galvanized sheet steel.

9. A laminate according to claim 7 or 8 wherein said modified elastomer or said composition comprises either one layer of a two layer structure or the middle of a three layer structure.



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